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Multi-elemental Analysis of Philippine Coffee Using X-ray Fluorescence Spectrometry for Varietal and Geographical Discrimination

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Abstract

Specialty coffee from specific regions in the Philippines holds high value, making it susceptible to adulteration. To ensure authenticity in terms of variety and origin, chemical analysis of coffee beans is crucial. This study, part of a larger multi-year project, used handheld X-ray Fluorescence (hXRF) to analyze 11 green coffee bean samples (Arabica, Robusta, Excelsa, and Liberica) from five regions (CAR, CALABARZON, Western Visayas, Central Visayas, and Caraga). Among the samples, high levels of potassium (K), magnesium (Mg), and sulfur (S) were observed, while arsenic (As), bismuth (Bi), and yttrium (Y) were detected in low amounts. Samples from each coffee variety and region exhibited distinct elemental compositions, allowing for differentiation. The study utilized a Random Forest classification model to predict coffee variety and geographical origin based on XRF-derived elemental data. As an estimation of performance, the OOB error and a test dataset was utilized, confirming the accuracy of the classification model. Furthermore, the MDS plots obtained for the varietal and geographical classification demonstrated a distinct clustering of samples. This suggests that multi-elemental profiles serve as effective discriminants and can be used as elemental fingerprints for identifying coffee variety and establishing provenance. Overall, the study highlights the potential of XRF-based multi-elemental profiling combined with machine learning algorithms as a promising method for coffee authentication and fraud detection.

Keywords: Elemental profiling, Geographical discrimination, Varietal discrimination, Machine Learning, X-ray Fluorescence Spectrometry

Introduction

Coffee, one of the most internationally traded products, has a deep-rooted history in the Philippines, where its tropical climate and position within the "Bean Belt" create ideal conditions for cultivating Arabica, Excelsa, Liberica, and Robusta varieties. Despite low production volumes, Philippine coffee has gained traction in foreign markets and continues to see strong local demand, especially for specialty coffee. This demand, driven by consumer appreciation for high-quality, uniquely flavored beans from specific origins, has boosted the industry’s growth and economic importance.

The specialty coffee scene in the Philippines is driven by consumer and producer interest in the entire coffee supply chain, from cultivation to brewing. As consumers become more aware of coffee origins and quality, they appreciate unique flavor profiles influenced by terroir—microclimates, soils, and altitude that impart distinct characteristics. This emphasis on single-origin coffee creates an opportunity for the Philippines to compete with other coffee-producing countries in quality and specialty coffee recognition.

Initiatives in transforming the Philippine coffee industry have escalated as non-government and government organizations provide training to farmers into becoming entrepreneurs and promote the coffee industry through coffee shop seminars and farm tours. Researchers are also interested in improving coffee farming practices with the aim of addressing problems at the coffee processing level, particularly in improving coffee bean quality and production in coffee-producing countries such as the Philippines (Byrareddy et. al., 2020; van Asten et. al., 2011; Ho et. al., 2017). Government-initiated projects such as the Philippine Coffee Industry Roadmap 2017-2022 have also been implemented with the aim of improving the coffee production in the Philippines by seven-fold, making our local coffee industry internationally competitive (DA, 2017). Through attaining a cost-competitive industry and aligning coffee production with global quality standards, farmers, roasters, and exporters will gain access towards better pricing opportunities and will benefit sustainably from increased demand.

The premium on authentic coffee offers Philippine farmers better pricing and market reach. As specialty coffees from specific regions gain value, demand from consumers and sellers is expected to grow, making it essential to protect both consumers and producers from adulteration and fraud through chemical analysis to ensure authenticity and traceability. Performing chemical analysis on Philippine coffee beans would allow us to understand the relationship between the elemental composition and geographical origin of the coffee beans. Consequently, this would help establish the traceability of Philippine coffee. Furthermore, by

ensuring the authenticity and traceability of Philippine coffee, the quality of coffee production in the Philippines will remain globally competitive.

One of the several factors that attract consumers is coffee quality. Coffee quality is defined by its chemical composition (Sualeh et. al., 2020), such as caffeine, chlorogenic acid (CGA), and trigonelline, physical attributes: length, weight, and size of coffee beans, and organoleptic characteristics: aroma, acidity, body, aftertaste, and balance (Bote & Vos, 2017), which are influenced by the coffee species, geographic origin, environmental conditions, and post-harvest processing methods. The environmental conditions that affect coffee bean quality include the amount of shade (Bote & Vos, 2017; Tolessa et. al., 2016; Worku et. al., 2017), amount and distribution of rainfall (Kath et. al., 2021), altitude (Worku et. al., 2017), temperature (Kath et. al., 2021), and soil characteristics (Yadessa et. al., 2020) including nitrogen levels (Bote & Vos, 2017). Along with these, post-harvest processing factors that affect coffee bean quality include the fermentation method (Peñuela-Martinez et. al., 2018), and the duration of fermentation (Zhang et. al., 2019).

The chemical composition and the physical attributes of coffee beans are influenced by the environmental conditions in which it was cultivated. Previous studies indicated that varying altitude and shade levels affect the caffeine, CGA, and sucrose concentration in green coffee beans (Worku et. al., 2018). Moreover, temperature and rainfall conditions also affect bean size with a high temperature being associated with larger beans and cooler temperatures with smaller beans (Kath et. al., 2021). Climatic conditions also affect the occurrence of defects in coffee beans. The negative effects on coffee quality arising from these factors reduce the profitability of coffee beans and may lead to cumulative impacts in the coffee industry, especially to small-scale farmers.

Developments in Coffee Research

As the production of specialty coffee beans gains momentum in the Philippine coffee industry, the need to understand how environmental factors and processing methods impact coffee bean quality becomes more critical. The coffee farming industry, with the help of the scientific community, has been exploring how these factors affect coffee quality in order to manage its negative impacts and make coffee production more sustainable and profitable for farmers all over the world. Aside from assessing the effect of environmental factors, agronomic practices have also been developed and studied to improve coffee farming such as improving irrigation management to increase coffee yield (Byrareddy et. al., 2020), intercropping (van Asten et. al., 2011), and synchronized system of coffee farming (Ho et. al., 2017).

The chemical nature of coffee beans and its effects on the coffee quality and flavor profile are one of the aspects of coffee production that need deeper understanding. With coffee becoming a premium product, it is important to investigate how factors such as geographical location and variety affect its chemical nature, not only for the purpose of improving coffee quality and farming methods, but for the purpose of authentication and traceability as well. Therefore, it is crucially relevant to identify reliable methods that will allow the characterization of elemental and chemical "fingerprints" present in different varieties of

Philippine coffee coming from different geographic origins. Recent studies have used the metabolomics approach in verifying the authenticity of different coffee beans including Civet coffee. These studies were aimed at identifying certain chemical markers associated with different coffee varieties and origins through comparing the ratios of the concentrations of the present volatile and non-volatile compounds such as caffeine, organic and phenolic acids, and carbocyclic sugars (Jumhawan et. al., 2013; Ongo et. al., 2020; Wei et. al, 2012). There are several instrumentation techniques that can be utilized for the analysis of metabolites in coffee beans. The most common techniques are gas chromatography coupled with mass spectrometry (GC-MS) as used by Ongo et. al. (2020) in the analysis of headspace (HS) metabolites, as well as NMR spectroscopy as used by Wei et al. (2014) in the determination of metabolites present in roasted coffee beans for sensory evaluation. While these methods have been proven successful in discriminating geographical origins of coffee beans through chemical composition, they are time-consuming and costly.

Similar studies that aim to establish the traceability of coffee beans have used the elemental composition of coffee beans as "fingerprints" to distinguish among coffees from different geographical origins or coffees of different types (Grembecka et al., 2007; Valentin & Watling, 2013; Antoine et al, 2015). Several studies have established the use of chemical composition of coffee beans for the geographical classification of coffee beans (Jumhawan et. al., 2013; Ongo et. al., 2020; Wei et. al, 2012). However, unlike the metabolomic composition of coffee beans which rapidly change due to the influence of changing weather conditions and other environmental factors, the elemental composition of coffee beans are more stable over time, and thus, is a more reliable criterion when it comes to determining chemical fingerprints and discriminating coffee beans based on variety and origin. Furthermore, Grembecka et al. (2007, as cited in Pohl et al., 2013) stated that the concentration differences in the elements found in coffee beans are much more distinctive than those known for the organic substances. A study by Grembecka et al. (2007) have used flame atomic absorption spectrometry (F-AAS) to measure the concentration of 14 elements in market coffee and distinguish arabica from robusta, ground from instant coffee, and their infusions. Valentin and Watling (2013) used solution based inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma emission spectroscopy (ICP-AE) to determine the concentrations of 59 elements in coffee samples from 15 countries and was able to classify the coffee according to their geographic origin. Another study by Antoine et al. (2015) utilized Neutron Activation Analysis (NAA) to determine the elemental composition among 24 coffee samples (ground, roasted, and soluble). Statistical analyses allowed the researchers to trace the geographic origins of Jamaican and international coffee, and distinguish between the different coffee types. These studies demonstrate the potential of using the elemental composition of coffee in conjunction with statistical treatment for the accurate determination of the geographical origin of coffee beans. While the application of elemental characterization methods is a relatively new technique in the establishment of coffee provenance and variety, it has been used in the analysis of other food products such as honey, wine, and tea (Bauyon et al., 2023; Fabani et al., 2010; Silva et al., 2021; Kanrar et al., 2022). Furthermore, Zhao et al. (as cited in Kanrar et al., 2022) stated that aside from the less cost, one of the advantages of utilizing elemental analysis for the discrimination of geographical origin in tea is the high stability of the mineral

elements in tea leaves in which it is not highly affected by the processing steps, storage time, and the analytical conditions involved.

X-ray Fluorescence Spectrometry

X-ray fluorescence spectrometry (XRF) is an analytical technique used for the quantitative and qualitative analysis of major, minor, and trace elements in a wide range of samples (Streli et al., 1999). The principle of XRF lies in the excitation of sample atoms by high-energy X-rays, which is followed by the emission of photons associated with a specific energy. The energy or wavelength associated with the emitted photon allows the qualitative analysis of the elements present in the sample. Likewise, the determination of the number of emitted photons allows the quantitative analysis of the sample.

Unlike other chemical analysis techniques, XRF spectrometry provides advantages such as the accurate and rapid analysis, multi-element analysis, and its ability to analyse the elemental composition of samples nondestructively (Choi & Sawada, 2022). Since it requires very minimal sample preparation and provides high analysis accuracy, it is commonly used as a method for environmental analysis (Kalnicky & Singhvi, 2001 as cited in Choi & Sawada, 2022) and in the research and development of materials (Gallen et al., 2014 as cited in Choi & Sawada, 2022). Field portable X-ray fluorescence (FPXRF) spectrometry have been applied as an analytical technique for the analysis of contaminant elements in environmental samples, such as metals in soils and sediments, thin films, and lead in paint (Kalnicky & Singhvi, 2001). A study by Sharma et al. (2014) used X-ray fluorescence to determine the elemental concentrations in soil and correlated it to soil pH. Its applications are not only limited to the in-field measurements of geological samples but also extends to the process control in mine and ore processing (Streli et al., 1999), and quality control – such as the analysis of impurities in Si-wafer surfaces at ultra-trace levels, and the multielement analysis of contaminants in soft drinks and poly(ethyleneterephthalate) (PET) containers (Zucchi et al., 2005). Moreover, its nondestructive nature makes it suitable for the analysis of fine art and archeological objects (Streli et al., 1999). The applications of XRF also broadly extend to the analysis of food samples. The study of Bauyon et al. (2023) utilized handheld X-ray fluorescence (hXRF) spectrometry combined with logistic regression analysis to detect C4 sugar adulteration in Philippine honey, with the aim of proposing a rapid, cost-effective, and more accessible alternative to resource-intensive and time-consuming analysis techniques.

Statement of the Problem

Establishing food traceability and authenticity through chemical characterization of coffee beans is essential to ensure the quality of Philippine coffees and protect the integrity of the local coffee market. With this, the study aims to determine the elemental composition of the 11 open-call samples of Philippine arabica, robusta, liberica, and excelsa coffee beans through X-ray Fluorescence Spectrometry. While established multi-elemental techniques such as ICP-MS and GC-MS are widely used for the characterization of coffee beans, these often require extensive sample preparation and can be costly (De Oliveira Costa et al., 2024; Valentin & Watling, 2013). On the other hand, XRF spectrometry provides a simple, rapid, and non-destructive analysis with minimal sample preparation (Bauyon et al., 2023). Due to these advantages, the study selected handheld-XRF with the aim of establishing a cost-effective and practical approach towards the varietal and geographical discrimination of coffee beans,

potentially benefiting farmers and the coffee industry through providing an accessible method for verifying product authenticity. With this analytical technique, the study aims to answer the following research questions:

1. What is the elemental composition of the coffee bean samples?
2. How are the elemental composition of the coffee samples related to the geographical origin of the coffee beans?
3. How are the elemental composition of the coffee samples related to the variety of the coffee beans?

Objectives of the Study

Specifically, the objectives of the research are:

1. To identify the elemental composition of the arabica, robusta, liberica, and excelsa coffee beans
2. To investigate on the possible correlation between the elemental composition and the geographic origin of the coffee beans
3. To determine coffee identifiers in relation to its elemental composition for the purpose of geographical and varietal classification

Significance of the Study

The coffee industry in the Philippines has developed and evolved as more people take interest in specialty coffee. With this, the whole coffee supply chain, starting from the farmers up to the baristas, collaborate to improve the quality of Philippine coffee and increase its value. As the potential of Philippine coffee is recognized, the industry is gearing towards not only delivering high-quality Philippine coffee to the local market but in introducing this to the international coffee market as well. With this, the need for research interventions that would facilitate the improvement of the quality and raising the value of Philippine coffee arises. As a high-value commodity, coffee beans become more vulnerable to adulteration and counterfeiting, imposing a threat to the Philippine coffee industry, the farmers, and the consumers. The results of the study will provide information that may be instrumental in the protection of the consumers and the producers by way of coffee bean authentication and through establishing the traceability of coffee beans. This ensures the legitimacy of the coffee beans that the consumers are getting, and provides farmers with protection against business competitors in the coffee industry who may take advantage of product mislabeling or adulteration for profit. Moreover, establishing our national coffee "identities" through multi-elemental fingerprinting is expected to foster increased national interest and moral in the coffee industry. The premium associated with coffee products that have established identities and fingerprints is envisioned to increase the revenue of the Philippine coffee industry and encourage more individuals to pursue the industry. Furthermore, studies concerning the metabolomic analysis on Philippine coffee beans for geographic discrimination have been conducted (Ongo et al., 2020), a comprehensive investigation on the multi-elemental composition of Philippine coffee beans from different regions is limited. The differences

between the elemental compositions of different varieties of coffee beans have also not been established due to limited studies.

Scope and Limitations

The study is limited to the investigation of elements present in 11 samples of coffee beans that were cultivated and harvested in the following regions in Philippines: Cordillera Administrative Region (CAR), CALABARZON (Region IV-A), Western Visayas (Region VI), Central Visayas (Region VII) and Caraga (Region XIII). There are many variables that are involved in the cultivation of coffee beans such as age of the tree, soil, and other factors, however this is outside of the scope of the project as the study is more focused on the fingerprint of coffee beans. The elemental profiling of the coffee beans was conducted by means of X-ray Fluorescence spectrometry. Furthermore, the study is limited to the development of a classification model through machine learning (random forest) for the prediction of the variety and origin of coffee beans based on its elemental composition. While we want to know the correlation of the multi elemental profile on other factors, it is outside the scope of the approved project by our funding agency.

Methods

Description of Sampling Regions

The green coffee bean samples used for analysis were acquired from open call submissions. A total of 11 different open call entries of 150 grams each were collected: 5 of which are Robusta, 3 Arabica, 2 Excelsa, and 1 Liberica. The samples of green coffee beans obtained originated from the following regions in the Philippines: Cordillera Administrative Region (CAR), CALABARZON (Region IV-A), Western Visayas (Region VI), Central Visayas (Region VII) and Caraga (Region XIII). These different coffee growing regions in the Philippines are comprised of a different climate, altitude, and soil conditions. Moreover, the fermentation and drying process of the open call samples also varies. The summary of information on the coffee bean samples are listed on Table 1.

Table 1.

Summary of Information on Coffee Bean Samples

#	Variety	Region	Address	Lat.	Lon.	Fermentation Process	Days of Drying
1	Robusta	XIII	Agusan Del Norte	8.7645	125.3295	Dry	5
2	Robusta	XIII	Agusan Del Norte	8.6653	125.4565	Dry	7
3	Excelsa	IV-A	Quezon	13.9450	121.4302	-	-
4	Excelsa	IV-A	Quezon	13.9450	121.4302	-	8
5	Liberica	IV-A	Quezon	13.9450	121.4302	-	-
6	Arabica	CAR	Baguio (80%), Benguet (20%)	16.4296	120.5484	Wet	-
7	Arabica	CAR	Baguio (80%), Benguet (20%)	16.4296	120.5484	Dry	-
8	Arabica	CAR	Baguio (80%), Benguet (20%)	16.4296	120.5484	Honey	-
9	Robusta	VI	Negros Occidental	10.6202	123.1570	-	7
10	Robusta	VII	Bohol	9.8793	124.0052	Wet	6
11	Robusta	IV-A	Quezon	13.9802	122.3600	-	3

Figure 1

Mapping of Open-call Samples from Different Regions in the Philippines

The Arabica green coffee bean samples were harvested in CAR, Excelsa and Liberica coffees were from CALABARZON, while the robusta coffees were from CALABARZON, Caraga, Western Visayas, and Central Visayas. The mapping of the open-call samples is presented in Figure 1.

Central Administrative Region (CAR)
CAR, located in northern Luzon, comprises six mountainous provinces, including Benguet, a significant area for Arabica coffee cultivation. The region's high elevation and clay loam soils support coffee farming, contributing 4.7% to the national Arabica coffee production in 2020. Despite occupying 6.2% of the country's land, CAR remains a vital coffee-growing area due to its suitable soil and climate (DA, 2017).

Western Visayas
Western Visayas includes six provinces, with Negros Occidental contributing notably to Robusta coffee production. The region, with 43% of its land dedicated to agriculture, has rich mineral resources and a favorable climate, supporting 8.1% of the national Robusta production in 2020 (DA, 2017). Western Visayas plays a vital role in the coffee industry through its robust agricultural base.

CALABARZON (Region IV-A)
Situated in central Luzon, CALABARZON is a key producer of Excelsa, Liberica, and Robusta coffee, especially in Quezon Province. With more than half of its land used for agriculture, the region's diverse landscape and abundant water sources enable the production of 8.6% of Excelsa, 12.7% of Liberica, and 2.1% of Robusta coffee in the Philippines (DA, 2017).

Caraga (Region XIII)
Located in northeast Mindanao, Caraga includes provinces such as Agusan Del Norte, where two of the Robusta coffee samples in the study is cultivated. The region's significant forest and agricultural lands contribute to its 3.9% share in national Robusta production (DA, 2017). Caraga's fertile soils and expansive agricultural zones support its role in the coffee sector.

Central Visayas (Region VII)
Central Visayas, particularly Bohol, supports coffee production, primarily for Robusta. With 66.5% of Bohol's land dedicated to agriculture, the region contributes to 1.9% of the Philippines' coffee production, leveraging its extensive agricultural land and suitable soil types like Ubay and Faraon clay (DA, 2017; Travero, 2016).

Table 2

Summary of Average Annual Temperature, Humidity, and Rainfall Per Region

Region	Average Temperature (°C)		Humidity (%)		Rainfall
	2021	2022	2021	2022	(mm)
Caraga (Region XIII)	28	28	86	84	2364.5
CALABARZON	29	29	75	76	493.4
CAR	27	28	82	79	1196.6
Western Visayas (Region VI)	28	27	80	81	1755.7
Central Visayas (Region VII)	28	28	80	82	1426.7

Sample Collection and Preparation

The objective of the analysis is to determine the elemental composition of the 11 Open Call green coffee bean samples through X-ray Fluorescence spectrometry. This study used an initial sample of 11 coffee beans as part of a broader multi-year study. This analysis provided initial results regarding the variability across coffee varieties and regions, allowing us to identify preliminary trends that will guide sampling strategies and focus areas in future phases of the multi-year study.

While the beans were not being analyzed, it was stored in proper conditions: away from sunlight and having a temperature of 18-25 degrees Celsius in order to maintain moisture content at 10-12%. Three steps were involved in the sample preparation: drying, pulverizing, and pelletizing.

The green coffee bean samples were oven dried using BIOBASE BOV-V230F Forced Air Drying Oven (Vertical Type) at 60 degrees Celsius for 26 hours. The drying temperature was maintained for 60 degrees Celsius during the course of 26 hours in order to lower the moisture content present in the beans (Coradi et. al., 2015). In a study by Soeswanto et. al. (2021), the most efficient temperature for drying coffee beans was observed to be at around 50°C in order for the prevention of microbial growth, preserve organoleptic characteristics (flavor and aroma), and quality. Afterwards, 2 to 3 grams each of the 11 green coffee bean samples were ground for 3 minutes using the Standard Ring Mill (SRM) from Rocklabs Limited, a pulverizer machine. The cone and quarter method was then used to obtained the ground samples for XRF analysis. The ground coffee beans were placed on top of a weighing paper inside an analytical balance during weighing in order to prevent contamination of the instrument and sample. The ground samples were then pelletized by applying 20 tons of pressure for 1 minute and 30 seconds (dwell) followed by a 30 second release using a 3636 X-

Press (SPEX SamplePrep, New Jersey). After successfully pelletizing all of the 11 samples, these were individually stored inside acetone-cleaned plastic sauce cups with cover until ready for handheld XRF (pXRF) analysis.

Analysis of Plant Standards

Before the analysis of coffee samples, 4 plant standards were analyzed in order to ascertain the accuracy of the instrument in getting the concentration of elements. The parameters set in the instrument can be found in Table 3. The 4 plant standards subjected to analysis were: Populus I (poplar leaf), Solanum Lycopersicum (tomato), Theobroma cacao (cacao leaf), and Medicago sativum (lucerne). Each plant standards were assigned with the following codes respectively: IPE-2018-2-2, IPE-2018-2-4, IPE-2018-3-2, and IPE-2018-3-4.

Table 3

Instrument parameters for the XRF Analysis of Plant Standards

Parameter	
Application	Geoexploration
Method	Automatic (Oxide3Phase)
Elapsed Time	30 seconds

Prior to analyzing the samples, the instrument underwent calibration to confirm its reliability and accuracy for the study. Once the elemental concentrations for each of the four plant standards were obtained (see Appendix I), these values were compared to certified values to assess the slope, offset, and correlation coefficient (R^2) (see Table 4). A correlation coefficient of 90% or higher was deemed acceptable. Eleven elements were detected in all four plant standards, yielding observed values expressed as a percentage by weight (wt%). These observed values, along with the certified values (see Appendix I), were input into the Bruker S1 Calibration Coefficient Calculation version 1.3 to derive the adjusted S1 results (corrected values). The correlation analysis indicates that the instrument demonstrates high accuracy and is capable of producing reliable data for analyzing coffee samples.

Table **4**

Correlation of Certified and Observed Plant Standard Values

Element	Slope	Offset	R^2
Ca	0.3959	0.4015	97.6%
Cu	0.6277	0.0001	99.8%
Fe	0.1255	0.0188	100%**
K	0.6321	-0.3825	99.0%
Mg	0.3754	0.0947	36.2%
Mn	0.2180	0.0012	99.7%
Zn	7.5429	0.0080	100%
Cr	18.0133	-0.0568	100%**
P	0.3483	0.0171	99.9%
Cl	0.325	0.0211	99.5%
Co	605.7500	-0.7681	100%**

Note. **involves < LOD values

Analysis of Green Coffee Samples

A total of 11 green coffee bean samples (from CAR, Region IV-A, Region VI, Region VII, and Region XIII) were analyzed using the S1 TITAN Model 800 Handheld XRF Spectrometer from BRUKER which has the capacity to detect elements from magnesium (Mg) up to uranium (U). The instrument was mounted in an upright position in its desktop stand. Each sample was directly placed on top of the desktop stand where the detection point of the pXRF can be found. The desktop stand was cleaned with kimwipes and ethanol for every sample change. The analysis of samples were performed in triplicates wherein 3 random points per pellet were scanned by the instrument. Table 9 shows the parameters set in the instrument for the analysis of the samples.

Table 5

Instrument Parameters For The XRF Analysis Of Green Coffee Bean Samples

Parameter	
Application	Geoexploration
Method	Automatic (Oxide3Phase)
Elapsed Time	90 seconds

The application used was geoexploration for the detection of inorganic elements with the method set as automatic which resulted in the use of Oxide3Phase. Each analysis ran a time of 90 seconds per point with a total of 5 minute runs per sample.

Statistical Analysis

Machine Learning (Random Forest) was used for the interpretation of the raw elemental data obtained from the analyses. The software used for the generation of random forest is RStudio (RStudio Desktop, Version 2022.07.2+576) . As defined by Hruska and Liu (2022), machine learning (ML) is "the study of computer algorithms that improve automatically through experience and by the usage of data." Machine learning approaches are classified into supervised, unsupervised, and reinforcement learning. In this study, a supervised learning method, specifically called random forest, was performed. Supervised learning methods such as random forest involves feeding a model with a well-structured data set that is composed of labeled variables and a specific outcome (Rezaei & Jabbari, 2022). Random forest is commonly used for both regression and classification problems (Rezaei & Jabbari, 2022). It relies on several decision tree algorithms and can be visualized as a combination of several decision trees concerned with a certain prediction. The outcome is then determined by the prediction made by the majority of decision trees. Random forest uses

bootstrapping or bagging in order to form different decision trees based on the data set. This process involves the selection of random subsets within a data set and training a decision tree using each of the subsets.

In the study, the variables used correspond to the concentrations of several elements present in each of the samples. Meanwhile, the factors to be predicted are the variety and the geographical origin of the coffee beans. As such, in order to decipher the relationship between the coffee variety and elemental composition, as well as the geographical origin and elemental composition, a classification algorithm was used. In creating the random forest, the number of trees and the number of variables tried (mtry) were optimized, such that the least possible Out-Of-Bag (OOB) estimate of error rate was obtained. Furthermore, in order to visualize the relationships between samples, a multidimensional scaling plot was generated. Multidimensional scaling (MDS) is an analytical technique that is utilized for exploring the structure of data based on their similarities and differences (Zhang & Takane, 2010). This represents samples as points in a multidimensional space, such that the points that are close to each other are similar, and those that are dissimilar are located far apart. Through the use of the MDS plot, the clustering of samples based on their variety and geographical origin were visualized.

Results and Discussion

A total of 21 elements (Mg, Al, P, S, Cl, K, Cr, Mn, Ni, Cu, Zn, As, Rb, Sr, Y, Nb, Pd, W, Pt, Bi, and U) were analyzed on the green coffee bean samples through X-ray fluorescence spectrometry. Among these, the major elements are Mg, P, S, and K, the minor elements are Cl, Cr, Mn, Ni, Cu, and Zn, and the trace elements are Al and As. Initially, the elements Mg, Al, and K were detected in their oxide forms: MgO, Al_2O_3, and K_2O, respectively. The concentrations of their oxide forms were converted to their corresponding elemental concentrations by dividing the oxide concentrations with the following values: 1.65 (for MgO), 1.89 (for Al_2O_3), and 1.205 (for K_2O). All of these elements were detected in the 11 samples, except for Pd and Pt, which were only detected a few times in the replicate analyses. Furthermore, the elements Ni, As, Y, Nb, W, Pt, Bi, and U were detected in low concentrations, having values below the limit of detection (<LOD) of the instrument for some samples. Among all the samples, the most abundant elements are K, Mg, and S, having an average concentration of 3.8021 (%wt), 0.8067 (%wt), and 0.5035 (%wt), respectively (Table 10). Meanwhile, the concentrations of As, Bi, and Y were amongst the lowest.

Table 6

Average Elemental Composition Of Green Coffee Bean Samples Obtained Through XRF Analysis

Element	Average Concentration (%wt)
Mg	0.8067273
Al	0.0895591
P	0.4748424
S	0.5034848
Cl	0.1698970
K	3.8021602
Cr	0.0051394
Mn	0.0089000
Ni	0.0001242
Cu	0.0033879
Zn	0.0006970
As	0.0000121
Rb	0.0031545
Sr	0.0032000
Y	0.0000212
Nb	0.0000424
Pd	0.0005758
W	0.0000485
Pt	0.0000455
Bi	0.0000182
U	0.0001000

Multi-Elemental Composition of Coffee Beans based on Variety

In the study, green coffee samples of different varieties (arabica, robusta, excelsa, and liberica) were subjected to multi-elemental analysis through XRF to determine their elemental composition. From this quantitative analysis, several differences in the major elements present were observed among the different coffee varieties (Figure 2).

It was observed that the Arabica green coffee samples have a higher concentration of P, Cr, Mn, Zn, and Nb amongst the other varieties. While it generated the highest concentration of Nb (7.77778 x10-5 %wt), the Nb content was relatively low and was below the LOD for the other varieties (Appendix Table A). The findings coincide with the study of Martin et al. (1998) which stated that green arabica coffees have a higher content of Mn compared to green robusta coffees. However, contrary to the findings which showed highest concentrations of P in green arabica coffees, Martin et al. (1998) observed that the P in arabica coffees tend to be lower than that of robusta coffee. Meanwhile, the concentration of Al, S, Cl, Rb, and S was the lowest in Arabica green coffees, and the concentration of As, Y, W, Pt, Bi, and U was below the LOD.

Robusta green coffee samples showed high concentrations of Cu, Ni, W, Pt, Bi, and U. Ni concentrations were relatively low in all varieties and was below the LOD in liberica samples. This is supported by the findings of Martin et al. (1998) which indicated that the concentration of Cu is higher in green robusta coffees than in green arabica coffees. Furthermore, the concentration of the elements W, Pt, Bi, U, were only high enough to be quantified in robusta coffees, and were below the LOD in the other varieties. It was also observed that Robusta green coffee samples tend to have the lowest Mg and Y (<LOD) concentrations. The trends observed with the Mn and Cu concentrations in green arabica and robusta coffees makes these elements the most effective discriminating factors between green arabica and robusta coffees (Martin et al., 1998).

The excelsa green coffee samples were observed to have the highest concentration in the following elements: S, K, Cl, As, and Y. While it showed the highest concentration of As and Y, these elements were present but were below the limit of detection in the arabica, robusta, and liberica varieties. Furthermore, it was found that the elements Cr, Mn, Cu, and Pd showed the lowest concentrations in excelsa coffees. Lastly, the elements Mg, Sr, Al, Rb, and Pb were found to be highest in liberica green coffee samples. Contrary to this, liberica green coffees showed the lowest concentrations of P, K, Zn, and As. Furthermore, the concentrations of Ni, Y, Nb, W, Pt, Bi, and U were below the LOD for this variety.

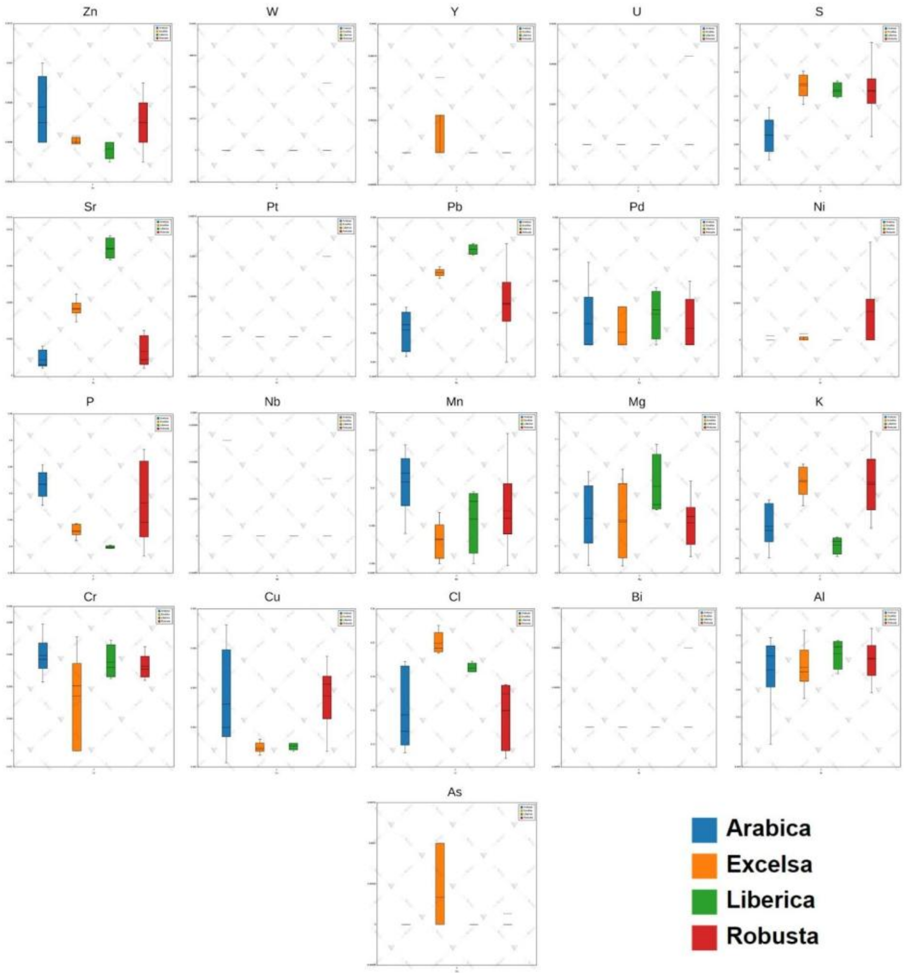

Figure 2

Boxplots Of The Element Contents Of Arabica, Excelsa, Liberica, And Robusta Green Coffee Bean Samples From The Philippines Determined By X-Ray Fluorescence Spectrometry

Multi-Elemental Composition of Coffee Beans based on Geographical Origin

The multi-elemental composition of coffee beans cultivated in different geographical origins are very distinctive (Gonzalvez et al., 2009 as cited in Pohl et al., 2013), and thus, can be used to establish coffee provenance. These differences are due to the influence of the geographical conditions (climate, temperature, altitude, humidity, and soil composition) and the growing environment on the elemental composition of coffee beans. In the study, the elemental composition of coffee beans cultivated from five different regions in the Philippines – namely, Cordillera Administrative Region (CAR), CALABARZON (Region IV-A), Western Visayas (Region VI), Central Visayas (Region VII) and Caraga (Region XIII) – were analyzed.

The findings of the XRF analysis showed that each of the sampling regions showed distinctive elements present in the coffee samples (Figure 3). In the Cordillera Administrative Region (CAR), for example, it was observed that green coffee bean samples had the highest concentrations of Cr, Mn, and Zn. It was reported that the concentrations of Mg, Cr and Zn, along with other elements (Ca, Cd, Cu, Fe, Mn, Ni, and Pb) in coffee beans are strongly

correlated with its concentrations in organic residues such as fertilizers (Dos Santos et al., 2009, 2010 as cited in Pohl et al., 2013). However, the concentrations of Al, K, and W were the lowest for this region.

Green coffee bean samples from CALABARZON showed the highest concentrations of S, Ni, Sr, Y, and U. The concentrations of the elements Y and U were high enough to be detected in samples from this region, but the concentrations of these elements in samples from the other regions were below the LOD. Similarly, the Ni concentration was the highest in this region but was below the LOD for CARAGA and Western Visayas. Contrary to these elements, the concentrations of Cr, Cu, and Bi were the lowest in the green coffee bean samples from CALABARZON.

The analysis of green coffee bean samples from Western Visayas (Region VI) revealed that green coffee beans from this region have highest concentrations of Al, K, As, Rb, Nb, and Bi, relative to the other regions. High concentrations of Al in green coffee beans may be influenced by environmental parameters, such as high pH in the soil in which the coffee is cultivated, which results to increased Al uptake by the coffee plant (Oleszczuk et al., 2007 as cited in Pohl et al., 2013). Arsenic (As) is a toxic metal and should not be present in food products. Relatively, the average concentration of As for samples from this region is low (1.66667 x10-5 %wt) and is below the LOD for CARAGA, CAR, and Central Visayas. Furthermore, the element Nb, was the highest in samples from Western Visayas but was below the LOD for CARAGA, CALABARZON, and Central Visayas samples. Likewise, the concentrations of the element Bi was also below the LOD for CALABARZON, CAR, and Central Visayas, and showed the lowest concentration in CARAGA. The elements Sr, Cl, Mn, and Zn, showed the lowest concentration in green coffees from Western Visayas.

Green coffee bean samples from Central Visayas (Region VII) showed the highest concentrations for the elements Mg, P, Cl, Pd, W, and Pt. Among these, the elements W and Pt were the most distinctive since it was only detected in samples from Central Visayas, and were below the LOD for the other regions. On the contrary, the element Rb showed the lowest concentrations in Central Visayas compared to other regions.

Lastly, for the samples from CARAGA region, only the element Cu showed the highest concentration relative to other regions. The increased content of Cu in coffee beans may be due to the influence of inorganic fertilizers used in coffee farms. Toxic elements such as Cu, Cd, and Zn contained in inorganic fertilizers may cause the increase of toxic metal concentrations in crop soil, and thus detected in agricultural products (Dos Santos et al, 2010). Furthermore, the increase in Cu content could also be caused by the addition of large amounts of organic matter during the flowering period. A higher uptake of Cd, Zn, and Cu in plants occur when high amounts of organic matter are added to soils (Dos Santos et al., 2009). Contrary to this, the elements Mg, P, and Sr showed the lowest concentrations in the CARAGA green coffee bean samples.

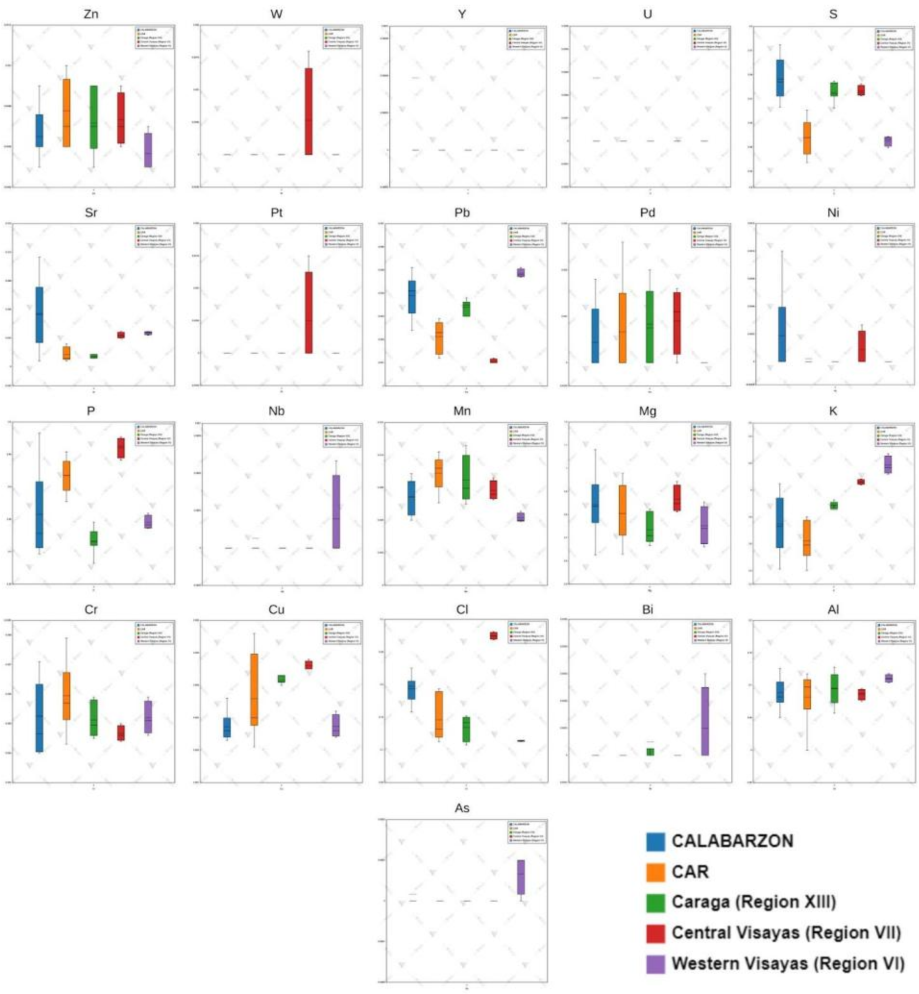

Figure 3

Boxplots Of The Element Contents Of Green Coffee Bean Samples From Calabarzon, CAR, Caraga, Central Visayas, And Western Visayas Regions In The Philippines Determined By X-Ray Fluorescence Spectrometry.

Machine Learning for the recognition of coffee origin and variety

In the study, machine learning was used to generate classification models in order to establish a tool for the predictive analysis of the variety (Arabica, Robusta, Liberica, and Excelsa) and geographical origin of coffee beans obtained from the following regions in the Philippines: Cordillera Administrative Region (CAR), CALABARZON (Region IV-A), Western Visayas (Region VI), Central Visayas (Region VII) and Caraga (Region XIII).

After conducting the elemental analysis, a Random Forest (RF) machine learning approach was used to categorize coffee beans according to their variety (Arabica, Robusta, Excelsa, and Liberica) and their geographic origin. RF was chosen due to its effectiveness in classification tasks through a combination of decision trees. The model was optimized by modifying the number of trees and the variables (mtry) considered at each split to minimize

the Out-Of-Bag (OOB) error rate. Furthermore, multidimensional scaling (MDS) plots were created to illustrate the relationships among the samples based on their elemental similarities.

Varietal Classification of Green Coffee using Machine Learning

For the generation of random forest for varietal classification, the dataset containing the concentrations of elements detected per variety was loaded in RStudio. Initially, the number of trees generated was set to 500, and the number of variables tried at each split was set to 6. However, this yielded an Out-Of-Bag (OOB) error rate of 6.06% from the misclassification of 2 Arabica samples as Robusta. The OOB estimate of error describes how well the decision trees are able to correctly predict the data points that are not included in the bagged data or training data (Rezaei & Jabbari, 2022). In order to optimize the number of trees, a plot of the error rate against the number trees was generated (Figure 4). It can be seen that the error rate decreases as the number of trees increases, but it still does not stabilize when there are 500 trees.

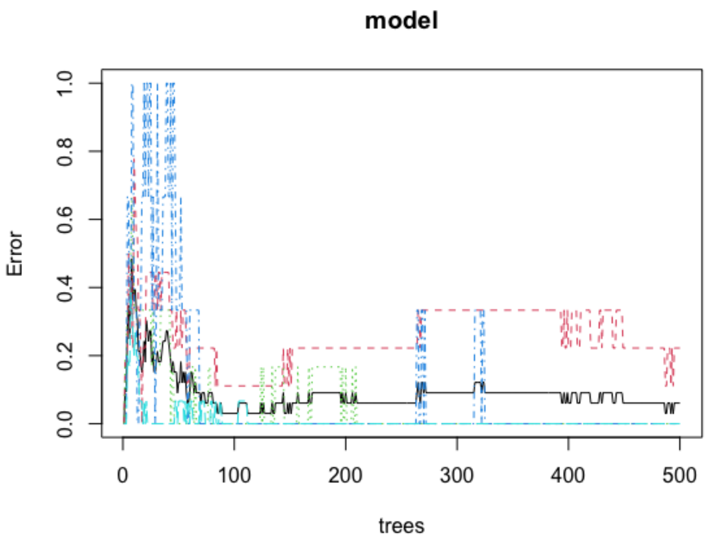

Figure 4

Random Forest Plot (Varietal Classification)

Furthermore, to optimize the number of variables tried at each split (mtry), a plot of the OOB error against the number of variables was generated (Figure 5). This showed that OOB error at mtry = 3, the OOB error is at 27.27%. Furthermore, increasing the mtry to 6 decreases the OOB error down to 3.03%. This OOB error rate stabilizes as the mtry is further increased to 12.

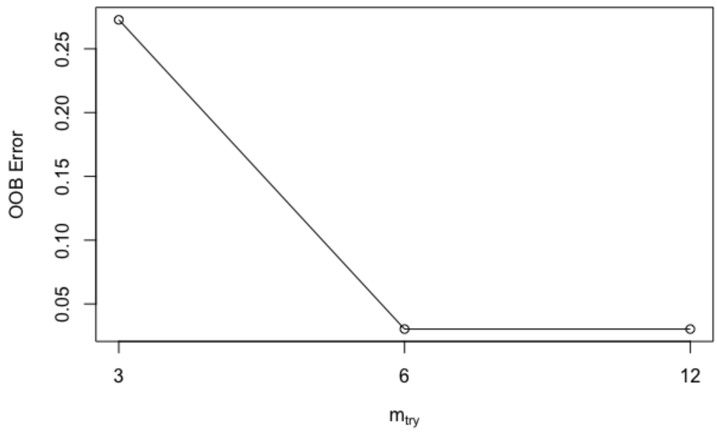

Figure 5
Plot Of OOB Error Against The Number Of Variables Tried At Each Split (Varietal Classification)

Based on these results, a refined classification model was generated using 700 trees, with $m_{try} = 12$. This resulted in a much decreased OOB estimate of error rate of 3.03% which resulted from the misclassification of 1 Arabica coffee as Robusta. The plot of the refined random forest is shown in Figure 6.

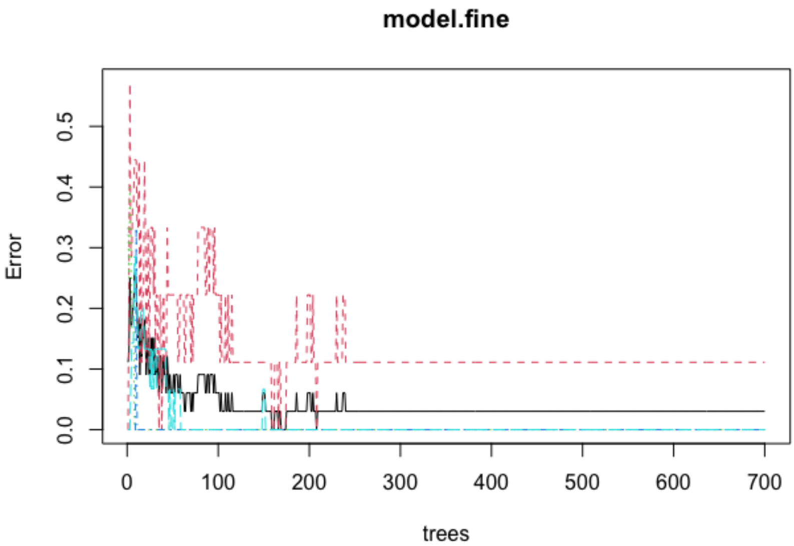

Figure 6
Refined Random Forest Plot (Varietal Classification)

The MDS plot for varietal classification (Figure 7) demonstrates distinct clustering of coffee samples according to variety, with Arabica, Excelsa, Liberica, and Robusta forming separate groups. This clear separation indicates that samples of the same variety share similar elemental compositions. The clustering supports the accuracy and reliability of the Random Forest classification model, which effectively leverages these elemental differences to predict coffee variety. The x-axis and y-axis capture 28.2% and 23% of the total variation, respectively, illustrating the main dimensions that account for the variability in elemental composition among the coffee varieties.

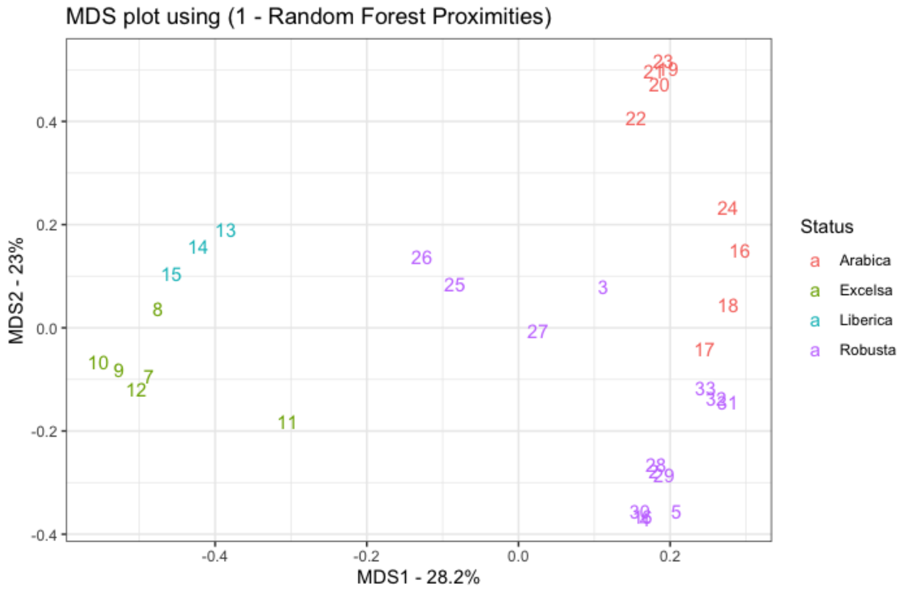

Figure 7

Multidimensional Scaling Plot for Varietal Classification

To assess the accuracy of the classification model, a test dataset was evaluated using the Random Forest algorithm. The predictions confirmed that the model accurately identified the coffee bean varieties based on their multi-elemental profiles.

Geographical Classification of Green Coffee using Machine Learning

For the generation of Random Forest for the geographical classification of green coffee beans, the dataset containing the concentration of elements detected in each of the samples obtained from the different regions was loaded in RStudio. Similar to the one generated for varietal classification, the program initially created a random forest containing 500 trees, having a total of 6 variables tried at each split. This generated an OOB error rate of 0%. This shows that the decision trees in the random forest correctly classified the data points that are not part of the training data. In order to see if the model could be further improved, a random forest plot was generated (Figure 8). As seen on the plot, the error decreases as the number of trees increases. However, error rate stabilizes at past 350 trees. Originally, the number of variables considered was set to 6. In order to see if further improvements can be made with this parameter, the OOB error was plotted against mtry (Figure 9). As seen on the plot, the OOB error is highest at mtry= 3 where it is 15.15%. This decreases down to 3.03% when mtry= 6 and further goes down to 0% when mtry= 12. Given that the optimal number of variables considered is 12, a refined random forest was generated and plotted. The optimized random forest consists of 500 trees, with mtry= 12. The plot of the refined random forest for geographical classification is illustrated in Figure 10. Compared to the previous random forest plot, the refined random forest plot indicated minimal error rates.

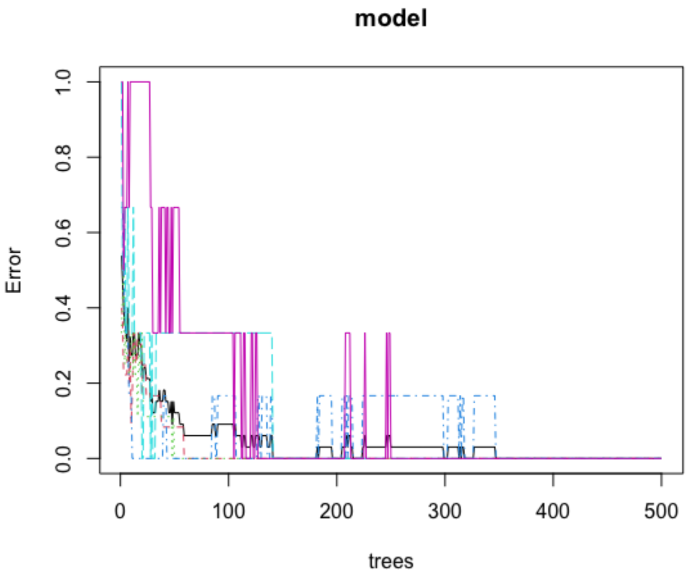

Figure 8
Random Forest Plot (Geographical Classification)

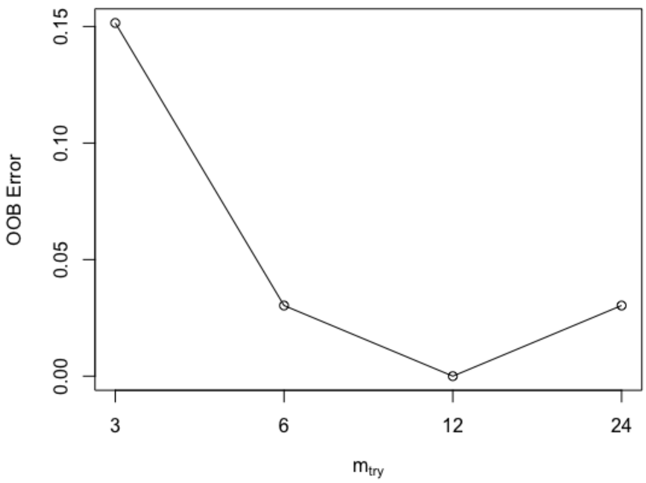

Figure 9
Plot Of OOB Error Against The Number Of Variables Tried At Each Split (Geographical Classification)

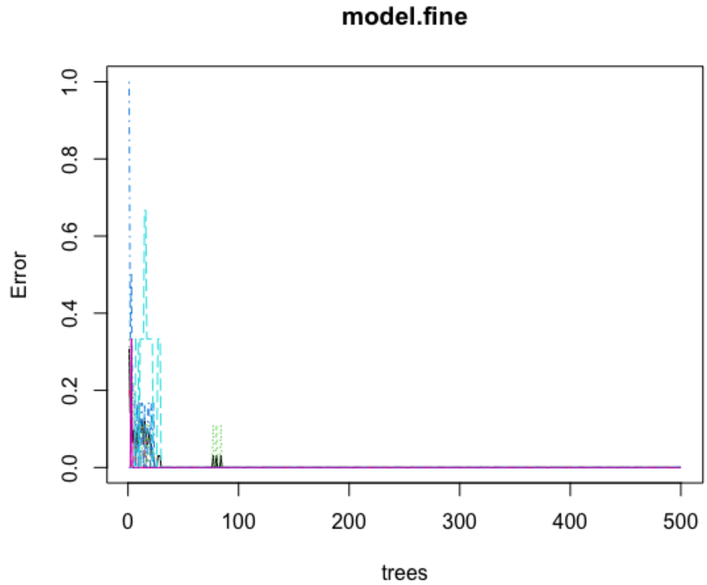

Figure 10
Refined Random Forest Plot (Geographical Classification)

An MDS plot was generated using the elemental data to visualize relationships between samples (Figure 11). Data points in close proximity represent similar samples, while those farther apart indicate greater differences. The MDS plot (Figure 11) illustrates clear clustering of coffee samples according to their geographical origin, with samples from the same region positioned closely together. This distinct grouping supports the reliability of the multi-elemental profiles in differentiating coffee origins, as samples from CALABARZON, CAR, Caraga, Central Visayas, and Western Visayas form separate clusters. The x-axis and y-axis explain 31.3% and 21% of the variance, respectively, highlighting the main dimensions of variability in the elemental composition data.

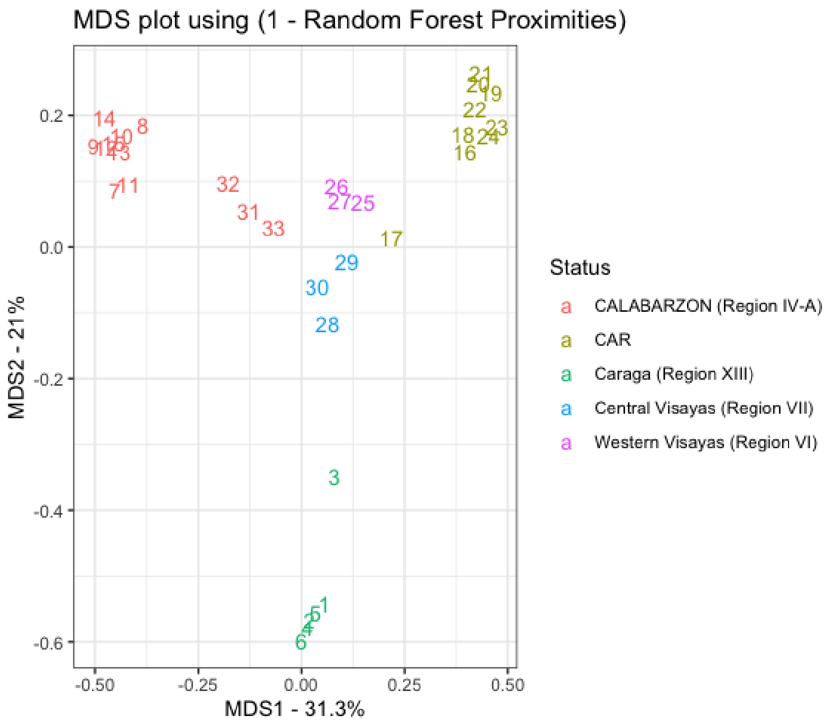

Figure 11
Multidimensional Scaling Plot (Geographical Classification)

To assess the accuracy of the classification model, it was evaluated with a test dataset in the Random Forest algorithm. The model successfully predicted the origin of the coffee bean samples, demonstrating high predictive accuracy based on their unique elemental profiles. These results confirm that the model effectively uses multi-elemental data to classify coffee beans by origin, highlighting its potential for applications in coffee authentication and traceability.

Conclusion and Recommendation

The XRF analysis of green coffee bean samples from different regions in the Philippines revealed the following elements: Mg, Al, P, S, Cl, K, Cr, Mn, Ni, Cu, Zn, As, Rb, Sr, Y, Nb, Pd, W, Pt, Bi, and U. Among the elements, K, Mg, and S were the most abundant, having the highest average concentrations in all of the samples. Furthermore, it was found that certain elements were distinctive for the four different varieties analyzed. The results showed that the concentration of P in arabica was higher than that of robusta coffees. Along with P, the elements Cr, Mn, and Zn were also highest in Arabica coffee samples, while Ni and Cu were the highest in Robusta samples. S, K, and Cl were found to be highest in Excelsa green coffee samples, while Mg, Sr, and Al were highest in Liberica green coffee samples. Moreover, the dominant elements in the green coffee beans also varied depending on the geographical origin. The element Cu was found to be highest in coffees from Caraga Region, while S, Ni, Sr, Y, and U were highest in coffee beans from CALABARZON.

For the coffee beans cultivated in CAR, the dominant elements were Cr, Mn, and Zn, while Al, K, As, Rb, Nb, Bi, were found to be highest in coffee beans from Western Visayas. Lastly, Mg, P, Cl, Pd, W, and Pt showed the highest concentrations in coffee beans from Central Visayas. With the multi-elemental data from the XRF analysis, machine learning techniques, specifically random forest (RF) was used to generate a classification model for the prediction of coffee variety (Arabica, Robusta, Excelsa, and Liberica) and origin (Caraga, CALABARZON, CAR, Western Visayas, and Central Visayas). The MDS plot obtained from the RF output indicated a clear clustering of the samples based on variety and origin. This clustering validates the elemental differences captured by the model, demonstrating that the elemental composition provides reliable fingerprints for the varietal and geographical classification of coffee beans. The application of machine learning to XRF data highlights the potential of the multi-elemental profile of coffee beans as effective discriminants, serving as unique elemental fingerprints for identifying coffee varieties and establishing coffee provenance.

In conclusion, this study demonstrates that the XRF-based multi-elemental profiling technique, when paired with machine learning algorithms like random forest, offers significant potential for coffee authentication and fraud detection. To gain a deeper understanding of the elemental patterns observed, future research should explore the relationship between the elemental composition of coffee beans and environmental factors

such as temperature, rainfall, humidity, and soil conditions. Additionally, increasing the sample size for each coffee variety and region will enhance the reliability of the results, leading to more robust and conclusive findings.

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APPENDIX I

Table A1

Elemental Composition of Plant Standard IPE-2018-2-2 (Populus I)

Element	Certified	Observed	Corrected
Ca	3.491	7.8067	3.492
Cu	9.547×10^{-4}	0.0013	8.80×10^{-4}
Fe	0.02270	0.0309	0.0227
K	0.9051	1.740	0.7172
Mg	0.4545	1.2489	0.5635
Mn	0.01259	0.0531	0.01
Zn	0.2274	0.029	0.22675
Cr	0.05668	0.0063	0.06
P	0.1575	0.3596	0.13708
Cl	0.4263	1.196	0.39
Co	0.4434	0.002	0.44

Table A2

Elemental Composition of Plant Standard IPE-2018-2-4 (Solanum Lycopersicum)

Element	Certified	Observed	Corrected
Ca	1.887	3.1053	1.631
Cu	9.427×10^{-4}	0.0014	9.42×10^{-4}
Fe	0.01728	< LOD	< LOD
K	3.812	6.467	3.705
Mg	0.5499	0.8810	0.4254
Mn	0.02041	0.0782	0.02
Zn	0.08862	0.0082	0.06986
Cr	0.8689	< LOD	< LOD

P	0.7116	1.9863	0.6736
Cl	0.2926	0.9421	0.32
Co	0.0385	< LOD	< LOD

Table A3

Elemental Composition of Plant Standard IPE-2018-3-2 (Theobroma cacao)

Element	Certified	Observed	Corrected
Ca	1.853	3.7082	1.870
Cu	2.373×10^{-3}	0.0037	2.386×10^{-3}
Fe	0.1616	< LOD	< LOD
K	1.603	3.405	1.770
Mg	0.6887	1.1253	0.5171
Mn	0.0499	0.2254	0.05
Zn	0.06403	0.0083	0.07061
Cr	0.05053	< LOD	< LOD
P	0.1776	0.4851	0.1881
Cl	0.05913	0.123	0.06
Co	0.6857	0.0024	0.69

Table A4

Elemental Composition of Plant Standard IPE-2018-3-4 (Medicago sativum)

Element	Certified	Observed	Corrected
Ca	1.365	3.0342	1.603
Cu	5.031×10^{-4}	0.0008	5.66×10^{-4}
Fe	0.02329	0.03560	0.0233
K	1.709	3.511	1.837
Mg	0.2419	0.8908	0.4291

Mn	0.0071	0.0333	0.01
Zn	0.06458	0.0092	0.0774
Cr	0.02966	0.0048	0.03
P	0.2509	0.6974	0.2601
Cl	0.6302	1.975	0.64
Co	0.04235	< LOD	< LOD

Bionote

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